

REMARKS

The amendments that have been made to the specification at pages 1, 9, 10, 12, 16, 27 and 28 correct obvious errors in the specification. Such errors would be readily discernible to a person skilled in the art. The amendment at page 9, line 9, to replace "600°C" with "300°C" is supported in the specification at various locations, for instance, page 6, line 19, page 8, line 31, and page 9, line 2. The temperature "300°C" is also recited at numerous locations in the various examples. Regarding Examples 24 and 26, it is obvious that Example 24 should refer to Example 23 and Example 26 should refer to Example 25.

The amendments that have been made to paragraphs [0018] and [0039] clarify the steps of the process of the invention. The fact that the dehydrated oxide ceramic is impregnated with a phosphating agent is supported, for example, by the specification at page 6, line 17. The fact that the heat treatment of the phosphate impregnated oxide ceramic at elevated temperatures seals the pores in the ceramic is supported, for example, in the specification at page 6, lines 17 through 24. Further support is provided at page 7, lines 7 to 11, of the specification. Yet further support is disclosed in the specification at page 8, lines 24 to 26.

Claim 1 has been amended to clarify the process steps of the invention. Support for the amendments that have been made to claim 1 can be found at the same locations in the specification as recited above in connection with the amendments that have been made to paragraphs [0018] and [0039] of the specification.

Entry of the foregoing amendments in this application prior to examination is respectfully solicited.

Respectfully submitted,

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VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification

[0003] Chemical reactivity in systems containing phosphoric acid or various forms of phosphates have received attention in scientific and patent literature. Particularly, the refractory applications and dental cements applications of *chemical bonding* (CB) of ceramics through phosphating have been disclosed. (See D. Kingery, "Fundamental Study of Phosphate Bonding in Refractories, Part I,II,III", *J. Am. Cer. Soc.* 33 (1950) 239-50; J. Cassidy, "Phosphate Bonding Then and Now", *Am. Cer. Soc. Bull.* 56 (1977) 640-43; J. Bothe and P. Brown, "Low Temperature Formation of Aluminum Orthophosphate", *J. Am. Cer. Soc.* 76 (1993) 362-68; and J. Bothe and P. Brown, "Reactivity of Alumina towards Phosphoric Acid", *J. Am. Cer. Soc.* 76 (1993) 2553-58.) For example, mixing aluminium oxide, or alumino-silicates, or zircon, or many other pure or mixed oxides (such as Cr<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>) with phosphoric acid H<sub>3</sub>PO<sub>4</sub> (PA) or monoaluminum phosphate Al(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, Al(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub>, (MAP) leads to reaction between the constituents and formation of chemical bond at relatively low temperatures of 200-400°C. These processes yield successful, commercial refractory materials. (See D. Kingery, "Fundamental Study of Phosphate Bonding in Refractories, Part I,II,III", *J. Am. Cer. Soc.* 33 (1950) 239-50.) The objective of these inventions was to produce monolithic ceramic while avoiding the usual high-temperature treatment (or "sintering") necessary to bond ceramic particles. Additionally, chemically bonded ceramics experience very small shrinkage during processing, i.e. size and shape of the resulting chemically bonded component is approximately the same as those of the mixed and pressed powder component.

[0018] In a specific embodiment, the invention involves a process of preparing a chemically bonded ceramic comprising: (a) as a first step, preparing a slurry of solvent and hydroxide ceramic; (b) as a second step, heat treating the hydroxide ceramic slurry at a temperature of between about 100 to 800°C to produce a dehydrated oxide ceramic; (c) as a third step, ~~phosphating impregnating~~ the dehydrated oxide ceramic with a phosphating agent to seal pores in the surface of the dehydrated oxide ceramic and produce a phosphated oxide ceramic; and (d) as a fourth step, heat treating the ~~phosphated phosphate~~ impregnated oxide ceramic at a temperature between about 200°C and about 1200°C to seal pores in the ceramic and produce a phosphated oxide ceramic.

powder to produce a mixed slurry; (b) applying said mixed slurry to a substrate to thereby coat the substrate with the ceramic hydroxide slurry; (c) heating the ceramic hydroxide coated substrate at a temperature up to about ~~600°C~~ 300°C to 1000°C to produce a ceramic metal oxide film on the substrate; and (d) sealing surface pores of the ceramic coating with a phosphorus containing ceramic sealant.

[0037] The key discovery of the subject invention is that the hydrated ceramic oxide, after calcination at mild temperature of 100°C to 1000°C, preferably about 200°C to 300°C, reacts rapidly with the phosphates and/or phosphoric acid and thus forms an excellent ceramic binder for other ceramic or metallic particles (fillers) present in the system. In applying the invention to the processing of ceramic coatings, the reaction is sufficiently rapid that the underlying metallic substrate is not exposed to damaging phosphating reactions. By using the above processes of the invention, non-permeable and crack-free thick ceramic coatings (from few µm, and up to several mm thick) have been successfully fabricated on variety of substrates, including steel, Ti, Cu, Al, Mg, fiber reinforced epoxy, ceramic, in simple spray painting/curing operation. The resulting coatings had bonding strength generally above 45 MPa, and surface hardness generally above 7 GPa, ~~and non-permeability to gases and liquids~~. The ceramic coatings produced according to the subject invention can be used to produce incremental wear and corrosion protection; dielectric coatings; thermal barrier coatings; bioactive coatings and also for sealing porous ceramic coatings and bulk materials, for improved corrosion and wear resistance. In another variant of the invention, high fraction of porosity may be allowed in thicker CB-CHC films to achieve low thermal conductivity (e.g. for thermal barrier coatings applications) or to achieve permeable membrane, useful for filtration of liquids or gases.

[0039] In a specific embodiment, the invention involves a process of preparing a chemically bonded ceramic comprising: (a) as a first step, preparing a slurry of solvent and hydroxide ceramic; (b) as a second step, heat treating the hydroxide ceramic slurry at a temperature of between about 100 to 800°C to produce a dehydrated oxide ceramic; (c) as a third step, ~~phosphating impregnating~~ the dehydrated oxide ceramic with a phosphating agent to seal pores in the surface of the dehydrated oxide ceramic and produce a ~~phosphated oxide ceramic~~; and (d) as a fourth step, heat treating the ~~phosphated phosphate impregnated~~ oxide ceramic at a temperature between about 200°C and about 1200°C to seal pores in the ceramic and produce a phosphated oxide ceramic.

temperature of the ceramics. The problems limiting the applications of ~~EHC~~ conventional ceramic processing for coating technology for corrosion and wear protection include cracking due to significant shrinkage. This problem has recently been partially addressed in the application of modified sol - gel technology for deposition of thick ceramic coatings (U.S. Patent No. 5,585,136, Barrow et al., Queens University). Thicker coatings (up to 6  $\mu\text{m}$  in single deposition and up to 200  $\mu\text{m}$  in multiple depositions) evidently did not crack upon drying because the gel phase contained up to about 90% wt. of the filler calcined (i.e. not shrinking upon heat treatment) ceramic. These coatings were however produced through complex sol-gel routes through dissolving salts, ~~organometallic~~ organometallic compounds, such as alkoxides, or carboxylates and ketones. The authors disclose in S. Kwon et al., "Sintering of Mixtures of Seeded Bohemite and Ultrafine Alpha Alumina", *J. Am. Cer. Soc.* 83 (2000) 82-88, and M. Kumagi et al., "Controlled Transformation and Sintering of a Bohemite Sol-Gel by Alpha Alumina Seeding", *J. Am. Cer. Soc.* 68 (1985) 500-505, a process where the stable dispersion of calcined ceramic in a sol is applied to a substrate, without a substantial temperature differential therebetween, so as to provide a coating thereon up to about 6  $\mu\text{m}$  thick. The resulting coating is subsequently fired so as to remove the organic constituents related to sol-gel processing. Even though active sol particles allow decrease of heat treatment temperature for the coatings disclosed in above mentioned U.S. Patent No. 5,585,136, weak bonding persists between coating and substrate, and permeability of the ceramic structure to gases and liquids persists (if porous). That is, even when the coatings were heat treated at temperatures up to 1000°C, residual porosity persists, thereby giving relatively low hardness for the coating and a high permeability to gases and liquids. The high temperature requirement for heat treatment is unacceptable for most metallic substrates due to melting (e.g. Al, Mg, Pb, Zn and others), or oxidation if heat treated in air, or microstructural deterioration. It has been disclosed in the recent U.S. Patent No. 6,284,682 B1 that this particular porosity and hardness problem can be addressed through use of a phosphate ceramic sealant by any of a number of techniques including impregnation, electrophoretic deposition, aluminum phosphate impregnation, phosphorus acid impregnation, and/or combinations of these treatments.

[0049] The reaction of orthophosphoric acid with aluminum oxide yields several different products depending on the type of alumina, the composition, reaction time and temperature. The combined effects of very high specific surface area and alumina concentration determine the kind and relative amounts of phosphates obtained by the reaction at a fixed temperature and time. The preferred system involves reaction of the alumina clusters

with well adhering, 10-3000 µm thick films for structural or functional applications. Deposition of thick, dense, fully ceramic films is accomplished in a simple painting-low temperature curing operation. Typical microstructure of the resulting coating is illustrated in Figure 1.

[0073] The hydroxide alumina – calcined alumina slurry was prepared and impregnated into porous carbon-carbon fiber composite, and heat treated as in Example ‡ 23. The sample was then impregnated with 30wt% phosphoric acid solution in water, in vacuum chamber for 30 min, and then fired again at 300°C for 30min. The resulting chemically bonded hydroxide ceramic carbon-carbon fiber composite had oxidation resistance three times higher and wear resistance eleven times higher as compared to the original carbon-carbon composite.

[0075] A mixture of aluminum hydroxide, alpha alumina, SiC and aluminum powder was prepared as in Example ‡ 25. After ball milling, the powder was mixed with 30% monoaluminum phosphate at volume ratio 10/1 of powder to solution, and then was pressed at 300°C for 20 min. The resulting consolidated ceramic-metal composite had tensile strength of about 27 MPa.

#### In the Claims

1.     (Once amended) A process of preparing a chemically bonded ceramic comprising:
  - (a) as a first step, preparing a slurry of solvent and hydroxide ceramic;
  - (b) as a second step, heat treating the hydroxide ceramic slurry at a temperature of between about 100 to 800°C to produce a dehydrated oxide ceramic;
  - (c) as a third step, ~~phosphating~~ impregnating the dehydrated oxide ceramic with a phosphating agent to ~~seal pores in the surface of the dehydrated oxide ceramic and produce a phosphated oxide ceramic~~; and
  - (d) as a fourth step, heat treating the ~~phosphated phosphate impregnated~~ oxide ceramic at a temperature between about 200°C and about 1200°C to seal pores in the ceramic and produce a phosphated oxide ceramic.